Adsorption of Dye by Natural and Modified Wood Dust

In partial fulfillment for the award of the Degree of

BACHELOR OF TECHNOLOGY

IN

CHEMICAL ENGINEERING

Report submitted

By

SUMIT KUMAR SINGH (110CH0404)

Under the guidance of

Prof. SANTANU PARIA

Department of Chemical Engineering

National Institute of Technology, Rourkela

Rourkela – 769008, Odisha, India

May, 2014

National Institute of Technology

Rourkela

CERTIFICATE

This is to certify that the report entitled, **"Adsorption of dye by natural and modified wood dust "** submitted by Sumit Kumar Singh in partial fulfillments for the requirements for the award of Bachelor of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

Date: 22/05/2014

Prof. Santanu Paria

Associate Professor

Department of Chemical Engineering

National Institute of Technology

Rourkela – 769008, Odisha

ACKNOWLEDGEMENT

In pursuit of this academic endeavor, I feel that I have been singularly fortunate; inspiration, guidance, direction, cooperation, love and care all came in my way in abundance and it seems almost an impossible task for me to acknowledge the same in adequate terms. Yes, I shall be failing in my duty if I do not record my profound sense of indebtedness and heartfelt gratitude to my supervisor Dr. Santanu Paria who guided and inspired me in pursuance of this work. His association will remain a beacon light to me throughout my career.

I owe a depth of gratitude to Prof. R.K.Singh, H.O.D, Department of Chemical Engineering, for all the facilities provided.

I want to acknowledge the support of all the faculty and friends of Chemical Engineering Department, NIT Rourkela.

Date: 22/05/2014 Sumit Kumar Singh

CONTENTS

List of Figures

List of Tables

Abstract

Presence of color impurity as an effluent poses a significant risk to the environment and human health. Industrial effluents mostly go untreated into the water streams and render it unfit for the use. Existing methods for effluent treatment such as charcoal adsorption are less effective, costly and less ecological friendly in nature. Hence a lot of research is going on throughout the globe for finding a low cost and efficient adsorbent. In the present work Pine wood dust is used as an adsorbent for Methylene Blue dye. This wood dust is modified with Acetic acid to increase its adsorption efficiency. Acetic acid reacts with the cellulose present in the wood dust and forms Cellulo-acetate at its surface which enhances its adsorption capacity. With modification of wood dust with Acetic acid the adsorption efficiency increased from 75% to 84% approximately. Adsorption efficiency of modified wood dust increased with decrease in pH. The adsorption process was found to be endothermic in nature. Hence it is an excellent adsorbent for removing the Methylene Blue dye from waste effluents of industries.

Chapter 1

Introduction

Dyes are widely used in food, textile, pharmaceuticals, cosmetics, printing, rubber, plastic and leather industries. More than ten thousand chemically different dyes are being produced around the world. The total dye stuff and dye intermediate produced is estimated to be around 70million kg per annum. Dyes are difficult to be biodegraded because of their complex molecular structure and hence once they enter the water they are difficult to remove. The industrial wastes of above industries are rich in dye content and hence pose a serious threat to the environment especially to aquatic life. Various harmful effects of dyes on our ecosystem are:

i) Dyes pose acute and chronic effects on the exposed organisms. The intensity of these effects varies depending on the time of exposure and the concentration of dyes.

ii) Dyes may absorb or reflect sunlight which enters the water bodies and hence may affect the growth of bacteria.

iii) Dyes are highly visible and even a small amount may cause abnormal colouration of water bodies which appears displeasing to eyes.

iv) Their complex molecular structures make them difficult to treat with common municipal treatment processes.

v) Some dyes consume the dissolved oxygen in water and affect the aquatic ecosystem.

Methylene Blue is mainly used in textile industries and has significance in pharmaceutical industry as well.

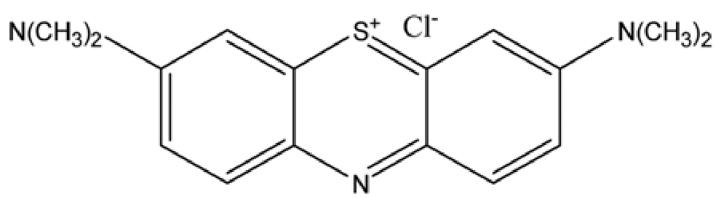


Fig. 1 Methylene Blue

It has various ill effects on eco system. Excessive amount of MB causes cardiovascular disorder, dizziness, fever, headache skin problem and anemia. MB is carcinogenic and very difficult to decompose. Hence removal of this dye from industrial waste is very important.

Various methods are used for removal of dyes like sedimentation, filtration, chemical oxidation, biological oxidation, electrocoagulation, ozonation, reverse osmosis and membrane filtration. But ‘adsorption’ has a prominent place because of its effectiveness and low cost. Most effective is the adsorption on activated carbon but because of its high cost industrialists generally does not dare to use it. Hence various low cost adsorbents have been found like alumina, clay, papaya seed, sawdust etc. Sawdust or Wood powder is very effective adsorbent as it does not swell and decompose in water. It is cheaply and abundantly available. It mostly contains lignin, cellulose, hemicellulose and functional groups like amide, phenolic, carboxyl and hydroxyl.

Various studies have been done on wood saw dust as an adsorbent but Pine wood dust modified with Acetic acid has not been studied.

In this work removal of MB dye by its adsorption on natural Pine Wood dust and Wood dust modified with Acetic acid was studied and compared. Various parameters like effect of temperature, effect of pH and effect of addition of electrolytes on the adsorption of modified wood dust was studied.

Chapter 2

Literature Review

2.1 Dye Structure:

Dye molecules generally comprise of two components:

1) The Chromophores: It is responsible for producing colour to the dye.

2) The Auxochromes: It enhances the affinity of dye towards fibers and supplements the chromophore part.

2.2 Dye Classification:

Dyes are classified mainly in following two groups:

1) Anionic dyes: They are used for nylon, wool, silk, modified acrylics etc.
e.g. Anthraquinone, Triphenylmethane, Azine, Xanthene, Nitroso etc.

2) Cationic dyes: They are used for paper, polyesters, polyacrylonitrile, modified nylons and in medicines.
e.g. Methylene Blue, Crystal Violet, Amaranth etc.

2.3 Adsorption with Pine saw dust:

Pine saw dust is mostly composed of cellulose and lignin. Pine tree is readily and cheaply available around the globe. Mostly the industries are located around forest areas away from the residential places where Pine tree is easily available.

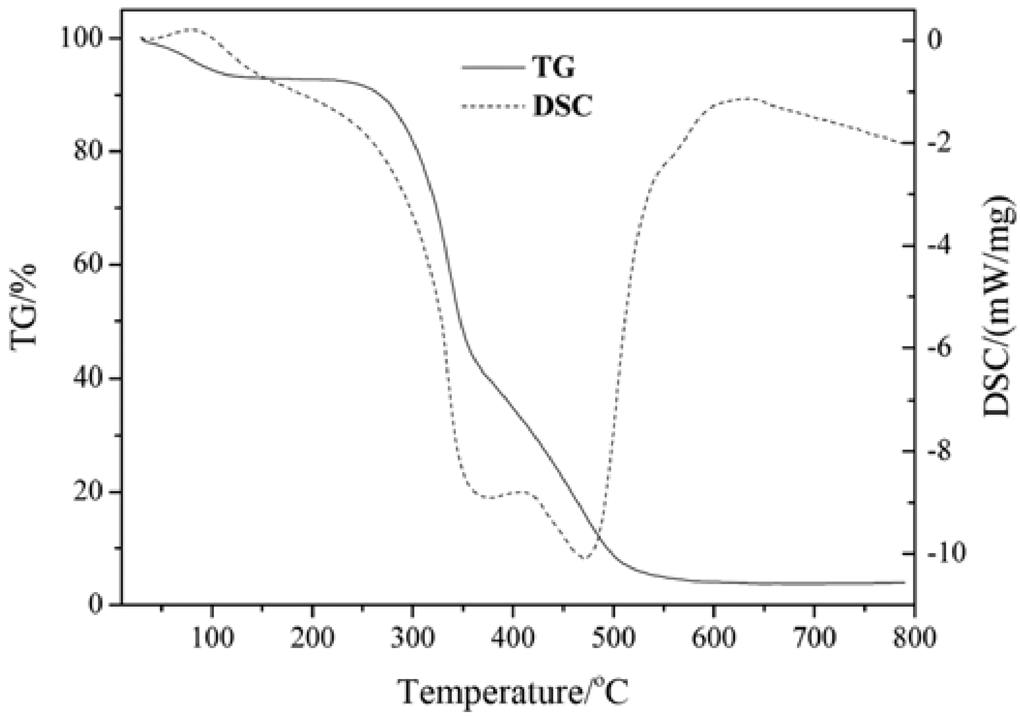
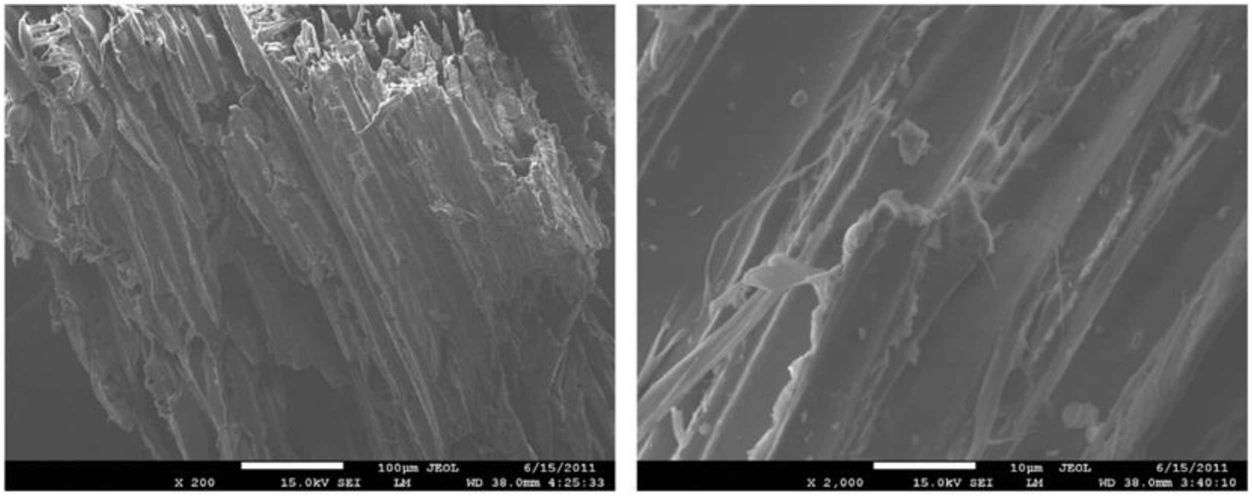


Fig. 2. Thermo gravimetric analysis (TGA) curves and differential scanning calorimetry (DSC) of Natural Pine wood dust [Ref: Korean J. Chem. Eng., 30(1), 111-122 (2013)]

The overall mass loss during TGA is divided into steps of moisture, cellulose and lignin. From fig 2.1 up to 190^o C the mass loss was 7.19% due to the removal of moisture from wood dust. From 190^o to 270^o C insignificant mass loss occurs. From 270^o to 375^o C mass loss of 52.79% of mass loss occurred. This shows the decomposition of cellulose matter and left water. Decomposition of lignin occurred in the range of 375^o to 520^o C with mass loss of 36.17% implying that this structure is more stable than cellulose.

In DSC curve max peaks were observed at 375^o and 470^o C by exothermic decomposition reaction of cellulose and lignin.



(a) **(b)**

Fig.3 SEM of Natural Pine sawdust (a)200X and (b)2000X. [Ref. Korean J. Chem. Eng. 30(1), 111 – 122 (2013)]

Scanning Electron Micrographs (SEM) shows that the surface texture of Natural Pine Wood dust is smooth with vertical grooves on the surface. Smooth fractured surface is due to presence of high amount of lignin in the compound middle lamella between cell walls and vertical grooves are due to removing all cell wall components, resulting in thinning of the cell wall.

Adsorption isotherms:

Adsorption is generally described through isotherms, that are the amount of adsorbate on the adsorbent as a function of pressure (for gases) or concentration (for liquids) at a constant temperature.

Freundlich isotherm:

It is an adsorption isotherm which relates concentration of solute on the surface of the adsorbent to the concentration of the solute in the liquid with which it is in contact. This model assumes that adsorption takes place on heterogeneous surface.

The linear form can be written as:

$\log q_e = \log k_f + (1/n)*\log C_e$

Where, k_f and n (dimensionless constants) are the Freundlich adsorption isotherm constants, which indicate the capacity and intensity of the adsorption, respectively.

Langmuir isotherm:

It relates the adsorption of molecules on a solid surface to gas pressure or concentration of a medium above the solid surface at a fixed temperature. It is based upon the fact that adsorption process occurs in monolayers.

The linear form of Langmuir expression:

$$1/q_e = 1/Q_o + 1/(bQ_oC_e)$$

Where C_e is the equilibrium concentration of dye solution (mg/L), q_e is the equilibrium capacity of dye on the adsorbent (mg/g), Q_o is the monolayer adsorption capacity of the adsorbent (mg/g), and b is the Langmuir adsorption constant (L/mg) and is related to the free energy of adsorption.

Chapter 3

Experimental Procedure

3.1 Materials: Methylene Blue stain was collected from Merck Specialties Private Limited, Mumbai. A Pine wood plank was obtained from a local carpentry shop in Lucknow, India. Acetic acid was also collected from Merck Specialties Private Limited.

3.2 Instrumentation: Orbital shaker and UV ray spectrophotometer were used in all the experiments. Centrifuge was used at 300 rpm for separation of supernatant from the solution.

3.3 Methods: A stalk solution of Methylene Blue (MB) of concentration 2.5 mM was prepared for all the experiments. The solution of MB was diluted with distilled water as required for the experiment. The plank of pine wood was converted into wood dust with use of eccentric sender machine in the Central Workshop at NIT Rourkela. A 0.2g weight of Pine wood dust and 10ml volume of the solution was fixed for all the experiments. Each sample was shaken in orbital shaker at 100rpm for required period of time. Samples were then centrifuged for 10 minutes at 300rpm, supernatant was separated and absorbance value was found by performing UV Spectroscopy. Similarly effect of initial dye concentration was observed on absorbance by Natural Wood-dust.

Acetic Acid was used for modification of Natural Wood-dust. Acetic Acid of 0.1M concentration was mixed with Natural Wood-dust in the ratio of 10:1 (V/W) and slurry was prepared. This slurry was stirred continuously for 30 minutes then dried in oven at 45 degree centigrade for 48 hours. Experiments were performed on this Modified Wood-dust as mentioned above.

3.3.1 Contact Time Study:

A solution of Methylene Blue was prepared of 0.25 mM concentration. Each sample contained 10ml of this MB solution and 0.2 g of Natural Wood dust was added in each sample. Samples were shaken in an Orbital shaker at 100rpm for 5, 10, 20, 30 and 45 minutes respectively then centrifuged for 10 minutes at 3000rpm. Supernatant was separated and UV Spectroscopy was performed and absorbance value was noted at 662.5nm wavelength.

3.3.2 Effect of Initial Dye Concentration:

10 ml solutions of Methylene Blue were taken of concentrations of 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8 mM. In each sample 0.2g of Natural Wood dust was added. Each sample was shaken in Orbital shaker for 30 minutes at 100rpm then centrifuged for 10 minutes at 3000rpm. Supernatant was separated and UV Spectroscopy was performed and absorbance value of each sample was noted at 662.5nm wavelength.

3.3.3 Effect in adsorption efficiency by Modified Pine Wood dust:

Natural Pine Wood dust was mixed with 0.1M Acetic acid solution in the ratio of 1:10 (w/v). This slurry was stirred continuously for 30 minutes and dried in Oven for 48 hours at 45^{o} C. 10 ml solutions of Methylene Blue of concentrations 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8 mM were taken and in each sample 0.2g of Modified Wood dust was added. Each sample was shaken in Orbital shaker for 30 minutes at 100rpm then centrifuged for 10 minutes at 3000rpm. Supernatant was separated and UV Spectroscopy of each sample was performed and absorbance value was noted at 662.5nm wavelength.

3.3.4 Effect in adsorption efficiency by addition of electrolytes:

0.2 g of natural wood dust was added in 10 ml of 0.25mM solution of MB. 1mM solution of electrolytes like $CaCl_2$, Na_2CO_3 and NaCl were added in different samples. Samples were shaken in Orbital shaker for 30 minutes at 100rpm then centrifuged for 10 minutes at 3000rpm. Supernatant was separated and UV Spectroscopy was performed and absorbance value was noted at 662.5nm wavelength.

3.3.5 Effect in adsorption efficiency with variation in pH:

pH of the solution was maintained by addition of proper concentration of HCl in the solution. The experiments were performed with 0.2g of Acetic acid modified wood dust and 10 ml of 0.25mM MB solution samples.

3.3.6 Effect of temperature:

Effect of temperature on adsorption efficiency of Acetic acid modified wood dust was observed by changing the temperature of the orbital shaker.

Chapter 4

Results & Discussion

4.1 Calibration Plot:

To determine the correlation between absorbance in UV-visible range and concentration for MB (Methylene Blue) dye experiments were done. In the experiment 10ml solution of MB of known concentrations were prepared followed by centrifugation and shaking. After the separation of the supernatant the absorbance was measured in UV-visible spectroscopy. To keep the value of absorption below 2 a suitable concentration range was chosen. A plot of concentration versus absorbance was obtained from the spectroscopy results. It is known that absorbance and concentration hold a linear relationship. So linear regression analysis was done to find the mathematical relation between absorbance and concentration. In the plot y is the absorbance at 662.5nm wavelength and x is the concentration. It is essential to find this relationship for the further experimentations.

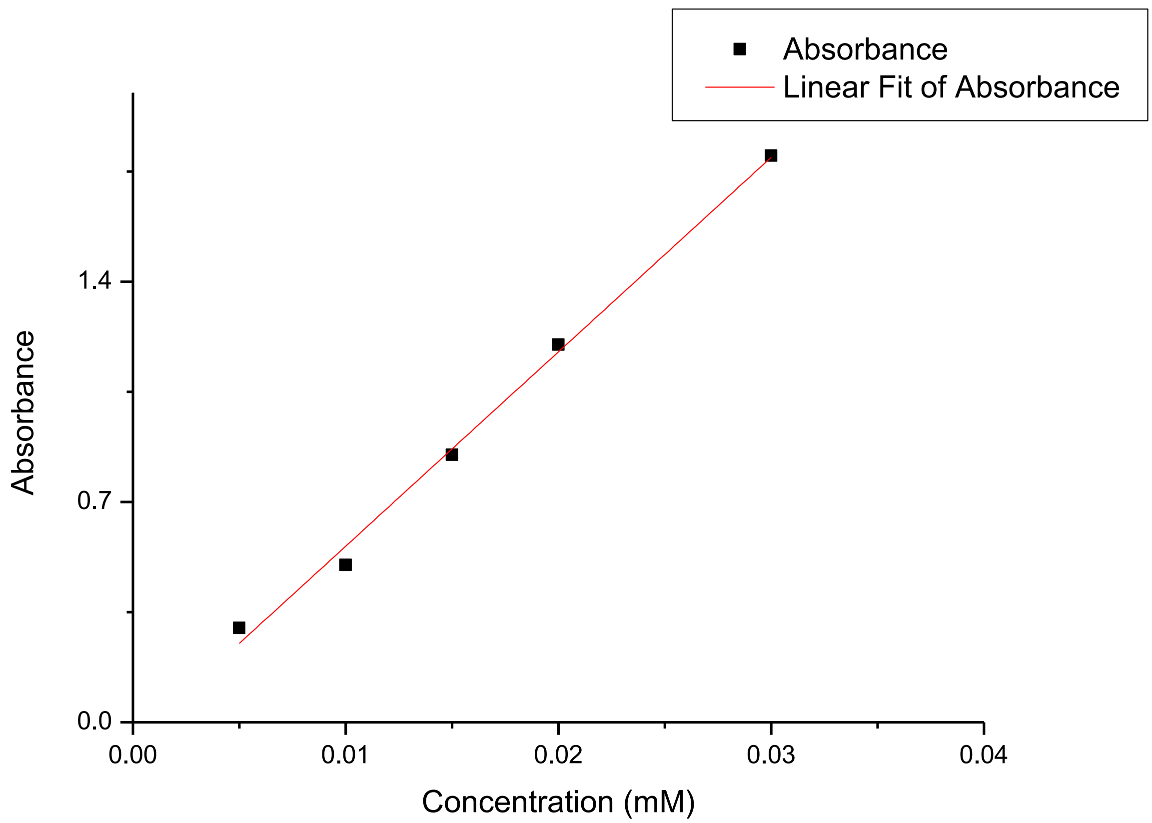


Fig. 4 [Calibration plot] Absorbance vs Concentration of MB

Relation obtained:

$Y = 61.75x$

$R^2 = 0.9965$

4.2 Contact Time Study:

The dependence of adsorption efficiency on time was studied from the data. Results showed that after 30 minutes approximately the absorbance value is almost constant that is there is no further adsorption of dye on wood dust. Therefore the saturation time of absorbance of MB on Pine Wood dust can be taken as 30 minutes.

The amount dye adsorbed per unit weight of adsorbent, q_e is calculated

$q_e = \{(C_o-C_e)/w\}*V$

where,

C_o = initial concentration of the solution,

C = concentration at equilibrium at time t,

W = weight of adsorbent used,

V = Volume of solution taken

Time (min)	Equilibrium concentration C_e (mg/l)	$q_e = \{(C_o-C_e)/w\}*V$
0	79.87	0
5	26.90	2.648
10	25.09	2.739
20	22.66	2.860
30	20.07	2.990
45	19.97	2.995

Table 1. Contact time study on natural Pine wood dust

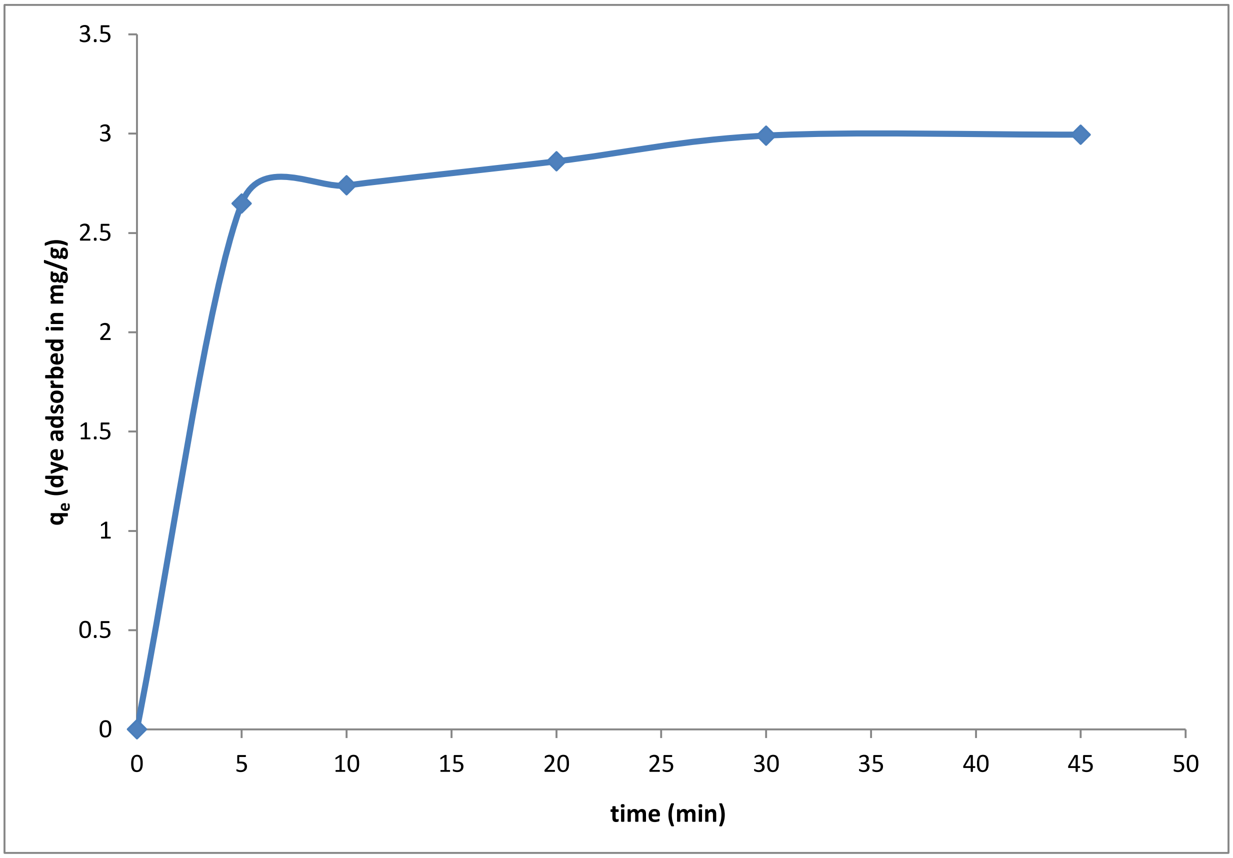


Fig 5. plot of q_e vs T for natural wood dust

This graph shows that rate of adsorption of dye is highest in first five minutes. After 30 minutes there is no further adsorption of MB on wood dust.

Time (min)	Concentration(mg/l), Ce	$q_e = \{(C_o - C_e)/w\}*V$
0	79.87	0
5	21.31	2.928
10	17.75	3.106
20	14.79	3.254
30	12.93	3.347
45	12.85	3.351

Table 2. Contact time study on modified Pine wood dust

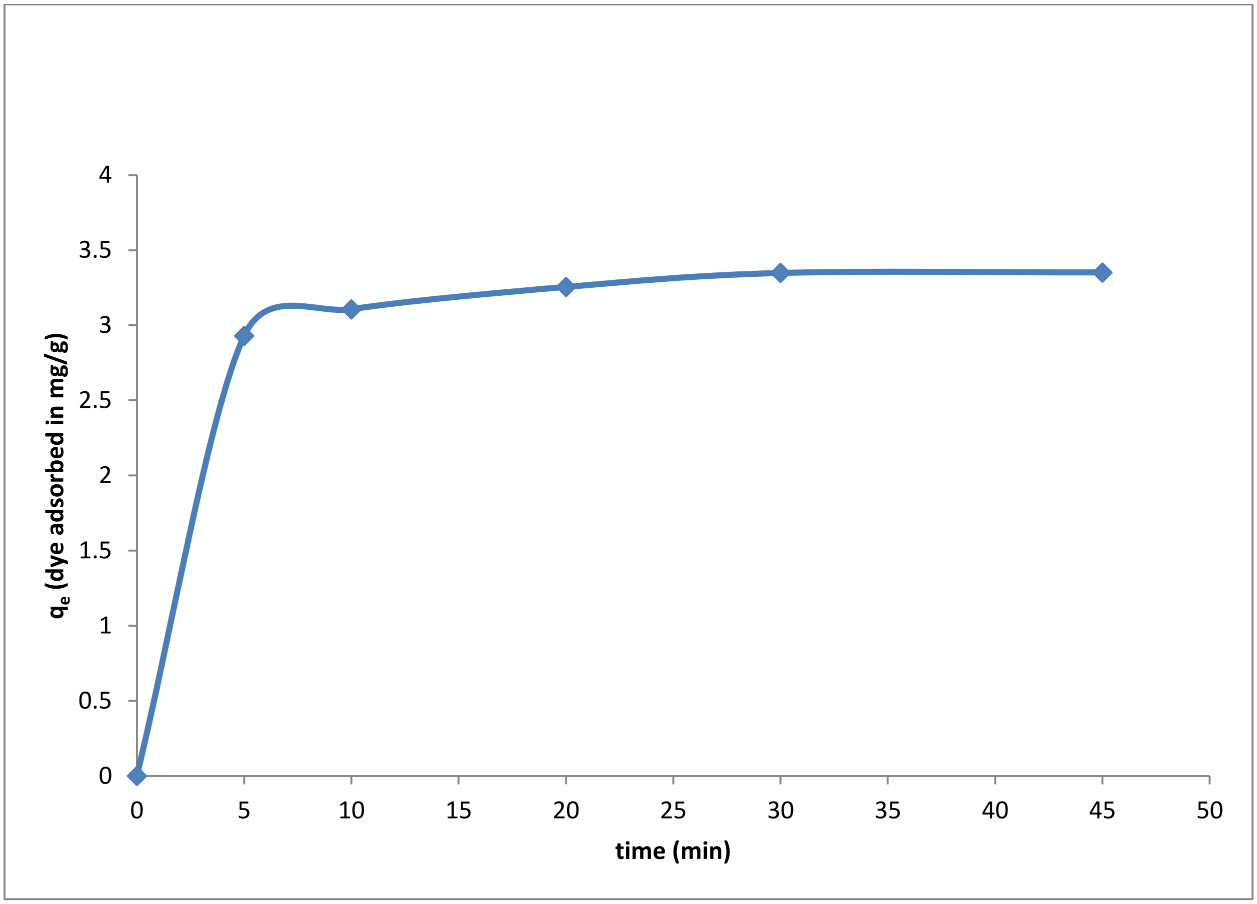


Fig 6. plot of q_e vs T for modified wood dust

Saturation time for Acetic acid modified wood dust is approximately 30 minutes. After 30 minutes there is almost no further adsorption.

The comparison between the contact times for natural and modified wood dust is given:

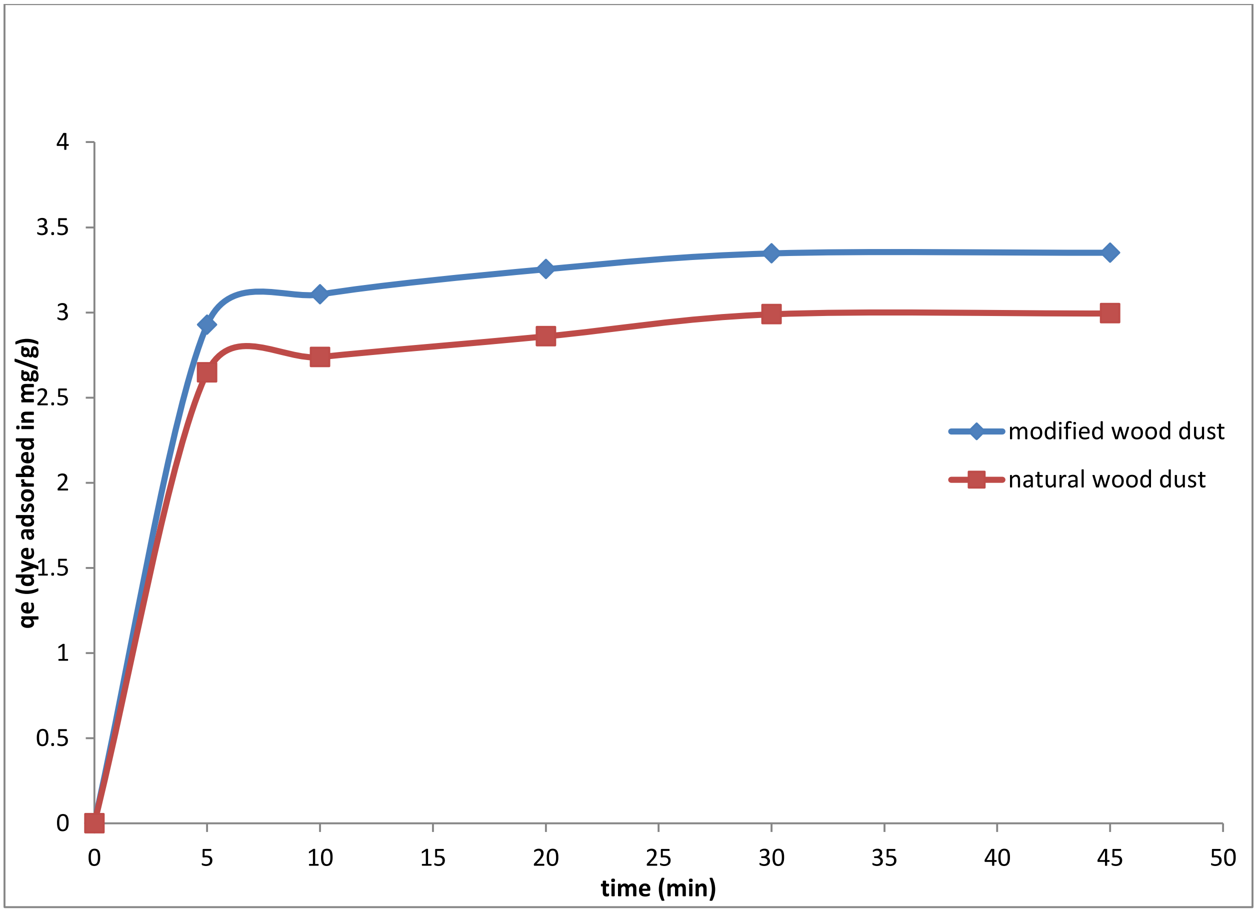


Fig. 7. Comparison of two contact time studies

It was observed that value of qe changed briskly for first five minutes, but after 30 minutes reached a saturation level. This can be explained by the fact that initially the surface of the dust was available for adsorption but as the time passed and after 30 minutes rate of adsorption was almost zero. At this point no more surface of the wood dust was free for adsorption. Thus the adsorption equilibrium was reached and 30 minutes was fixed as the optimum time for further experiments. The amount of dye adsorbed was increased by 10.74% with use of Acetic acid modified wood dust and the rate of adsorption of dye was also higher for modified wood dust.

4.3 Effect of initial dye concentration:

No significant variation in absorbance value is noted after 0.4mM concentration of MB. Hence it can be assumed to be the saturation limit for 0.2g of adsorbent.

Initial concentration (mM)	Equilibrium concentration (Ce) after 30 mins (mg/l)	q_e (mg/g)	% removal of Methylene Blue
.05	3.99	0.59	71.30
0.1	7.68	1.21	74.01
0.2	15.36	2.43	74.83
0.3	23.00	3.64	76.00
0.4	31.58	3.59	76.49
0.5	37.82	3.68	76.60
0.6	46.50	3.68	76.84
0.7	49.23	3.72	76.70
0.8	53.80	3.69	76.74

Table 3. Effect of initial dye concentration for natural wood dust

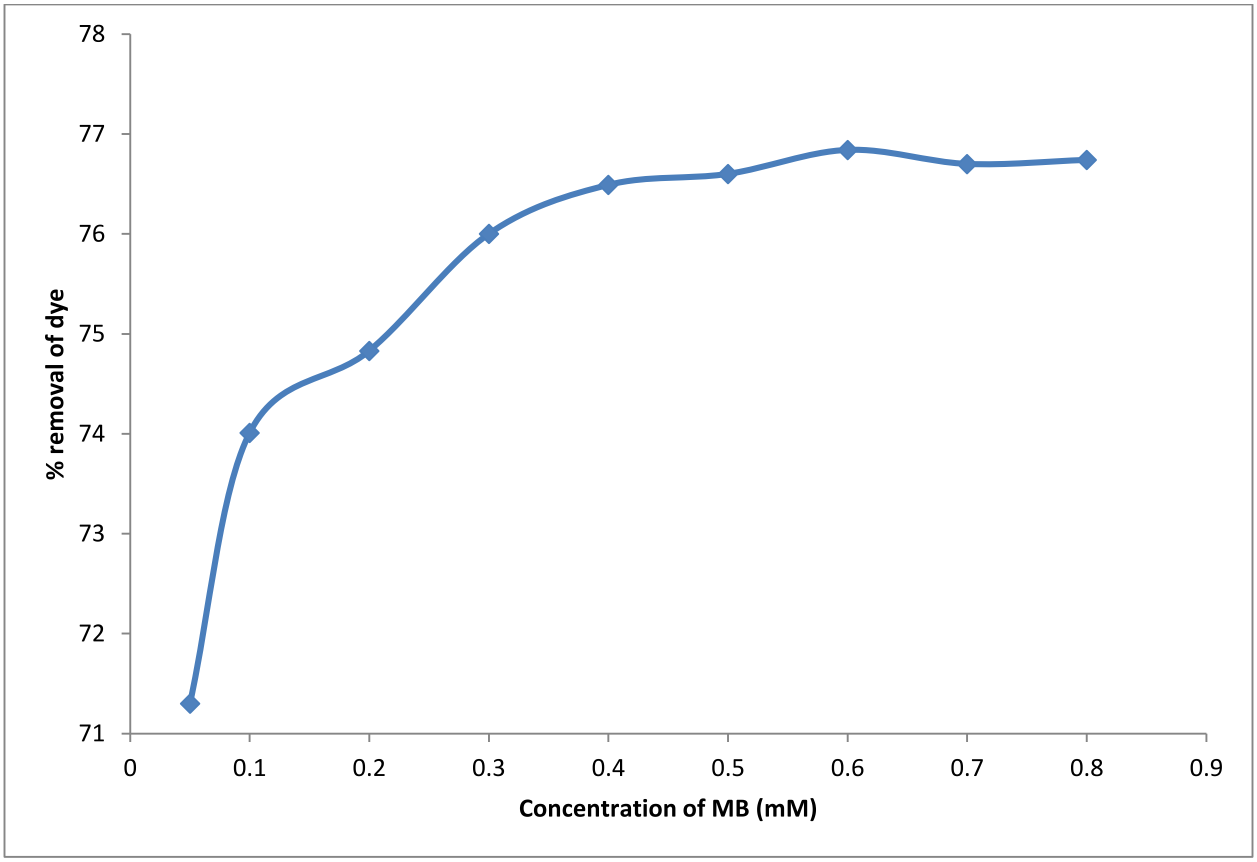


Fig 8. % removal of dye vs dosage on natural wood dust

Initial concentration (mM)	Equilibrium concentration (Ce) after 30 mins (mg/l)	q_e (mg/g)	% removal of Methylene Blue
.05	3.41	0.63	78.60
0.1	6.55	1.27	79.50
0.2	11.29	3.54	82.32
0.3	14.57	3.81	84.80
0.4	19.63	3.99	84.64
0.5	23.96	4.02	85.01
0.6	28.94	3.96	84.91
0.7	34.03	4.07	84.88
0.8	38.70	4.04	84.86

Table 4. Effect of initial dye concentration on modified wood dust

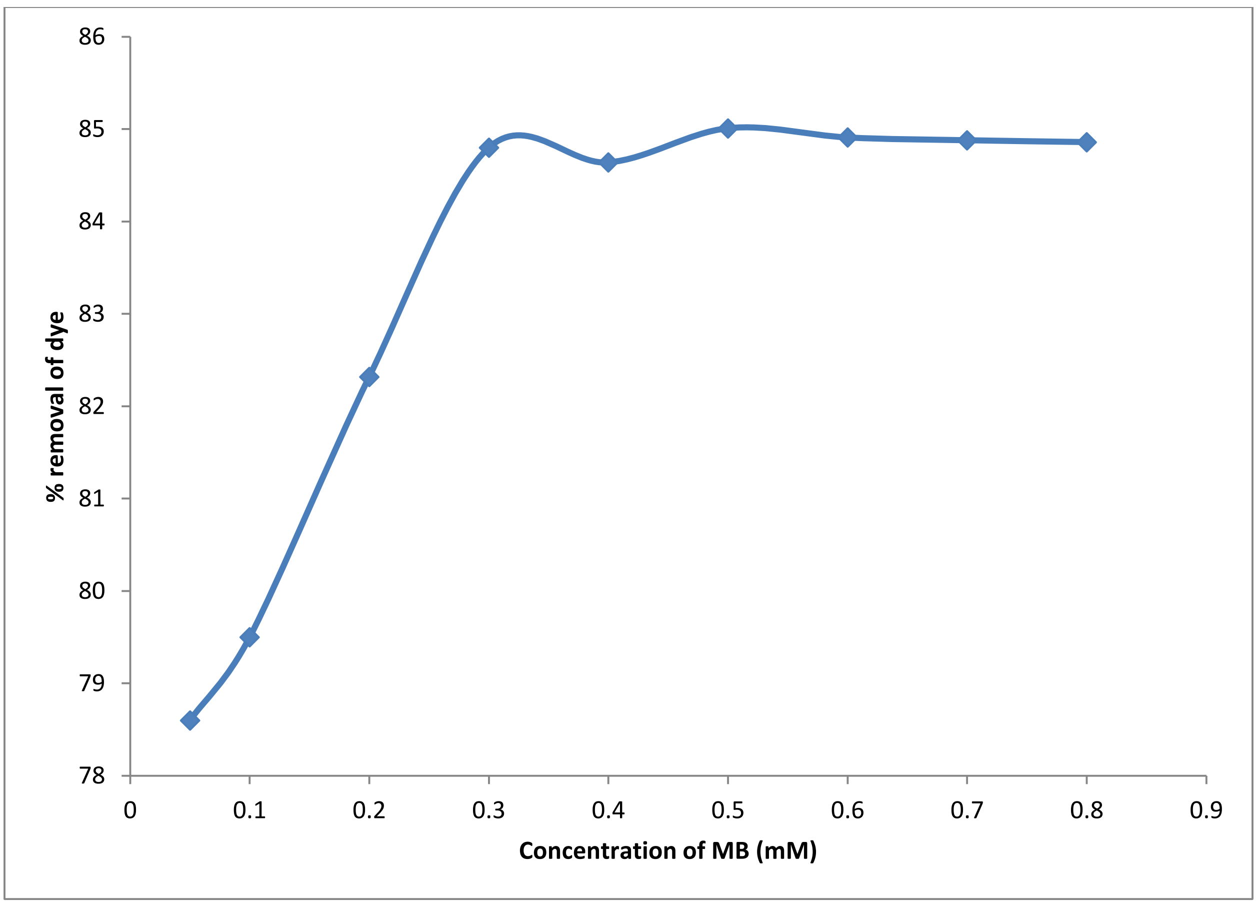


Fig. 9. % removal of dye vs dosage for modified wood dust

It was found that the percentage of removal of dye increased from around 76% to 85% approximately with the use of Acetic acid modified wood dust.

Adsorption Isotherms:

Adsorption isotherms provide an equilibrium relationship between amount of adsorbate adsorbed on the surface of the adsorbent and its equilibrium concentration in the solution. In literature various adsorption isotherms are available to fit the experimental data. In this study Freundlich and Langmuir isotherm models were studied.

Freundlich Isotherm model:

The linear form of Freundlich model is:

$\ln q_e = \ln k_f + (1/n)*\ln C_e$

where 'k_f' and 'n' are dimensionless Freundlich isotherm constants indicating the capacity and intensity of the adsorption.

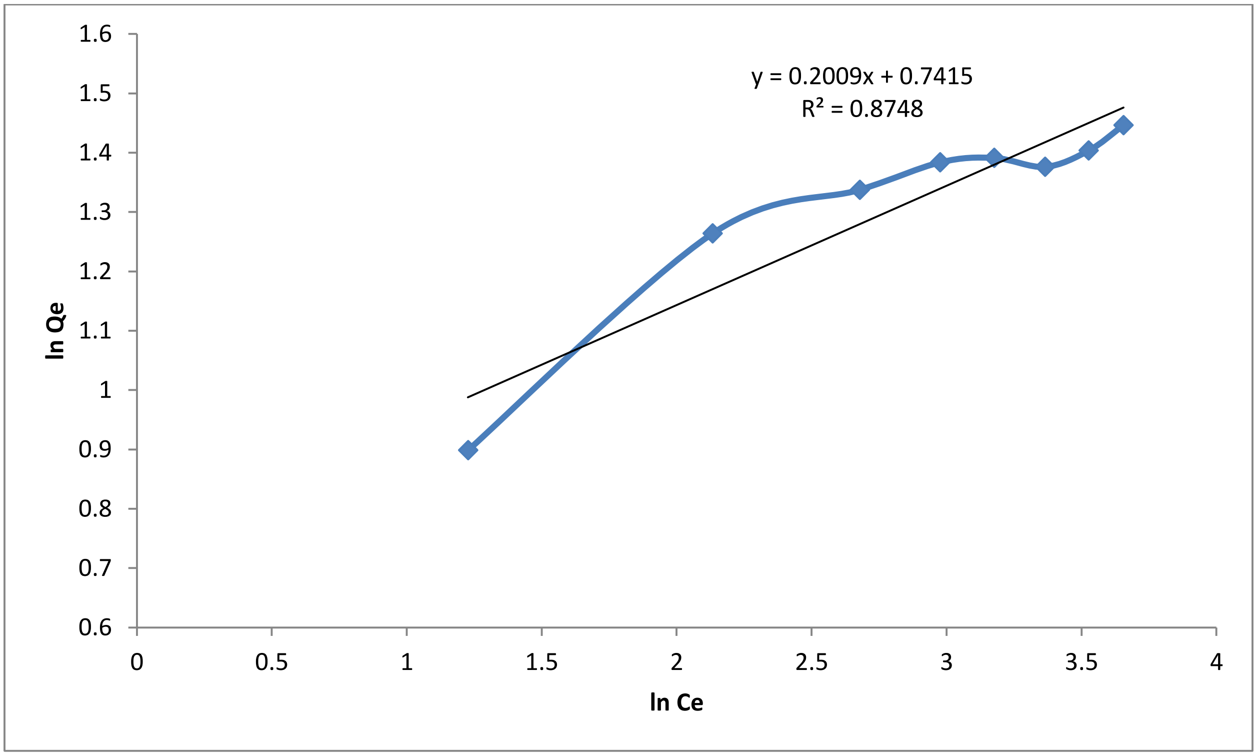


Fig 10. Freundlich model

$Y = 0.2009x + 0.7415$

$R^2 = 0.8748$

From the graph value of n was found to be 2.285 and k_f was found to be 1.69. Since the value of n is greater than 1, it is not a suitable model for the current adsorption process.

Langmuir Isotherm model:

Linear form of Langmuir expression is:

$1/q_e = 1/Q_o + 1/(bQ_oC_e)$

Where Q_o is the monolayer adsorption capacity of the adsorbent (mg/g) and b is the Langmuir adsorption constant (L/mg) and is related to the free energy of adsorption.

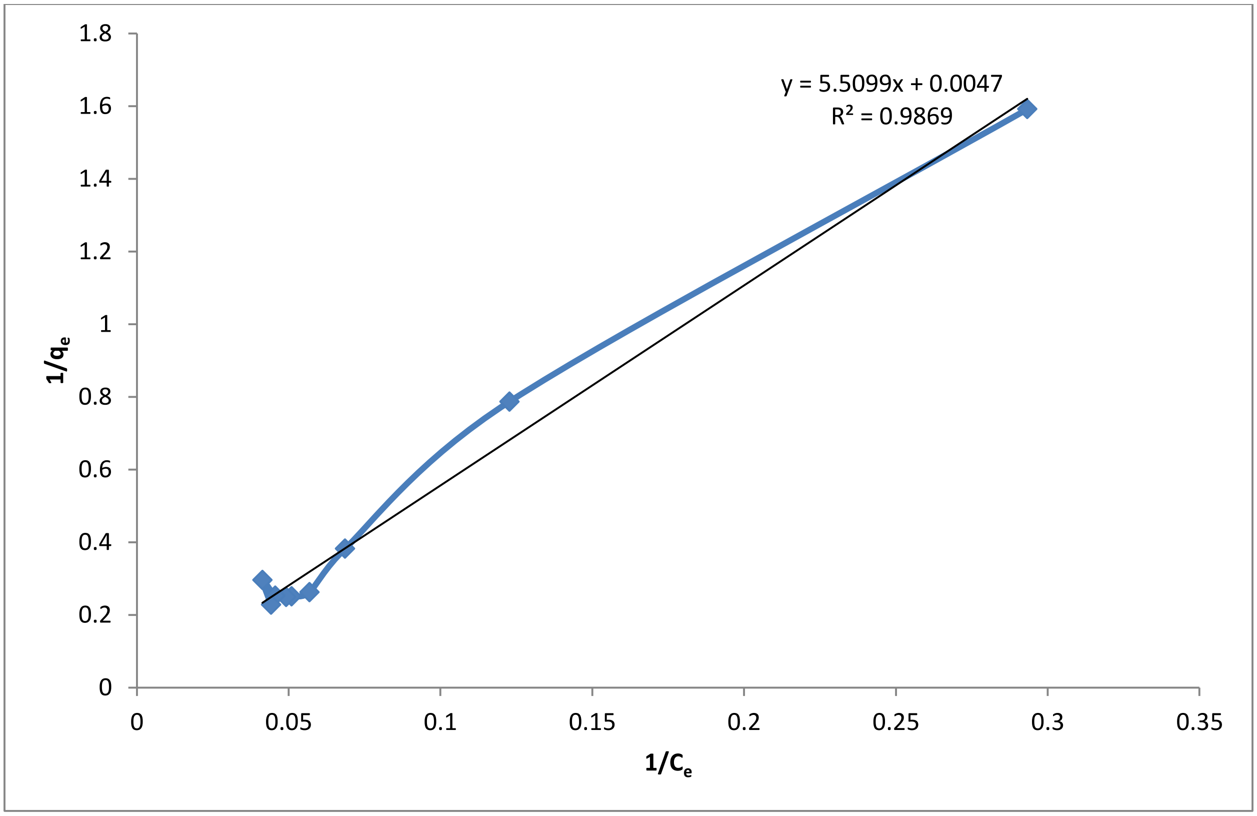


Fig 11. Langmuir model

From graph value of Q_o = 21.27 mg/g,

And b = 0.853 l/mg

Since value of R^2 is close to one, hence Langmuir model fits with experimental data.

4.5 Effect of electrolytes addition:

Sample	**% removal of dye**
Modified wood dust	83.82
Modified wood dust + $CaCl_2$	80.23
Modified wood dust + Na_2CO_3	80.22
Modified wood dust + NaCl	68.02

Table 5. Effect of addition of electrolytes

It was observed that addition of electrolytes decreased the adsorption efficiency of the Acetic acid modified wood dust adsorbent. Percentage of removal of MB from its solution decreased with addition of electrolytes.

4.6 Effect of pH on adsorption efficiency :

pH	C_e, concentration at equilibrium (mg/l)	q_e, (mg/g)	% removal of dye
7.0	2.500	3.347	83.80
5.5	2.485	3.351	83.93
4.5	2.238	3.416	85.54
3.5	2.284	3.424	85.75
3.0	1.969	3.484	86.84

Table 6. Effect of pH on adsorption efficiency of wood dust

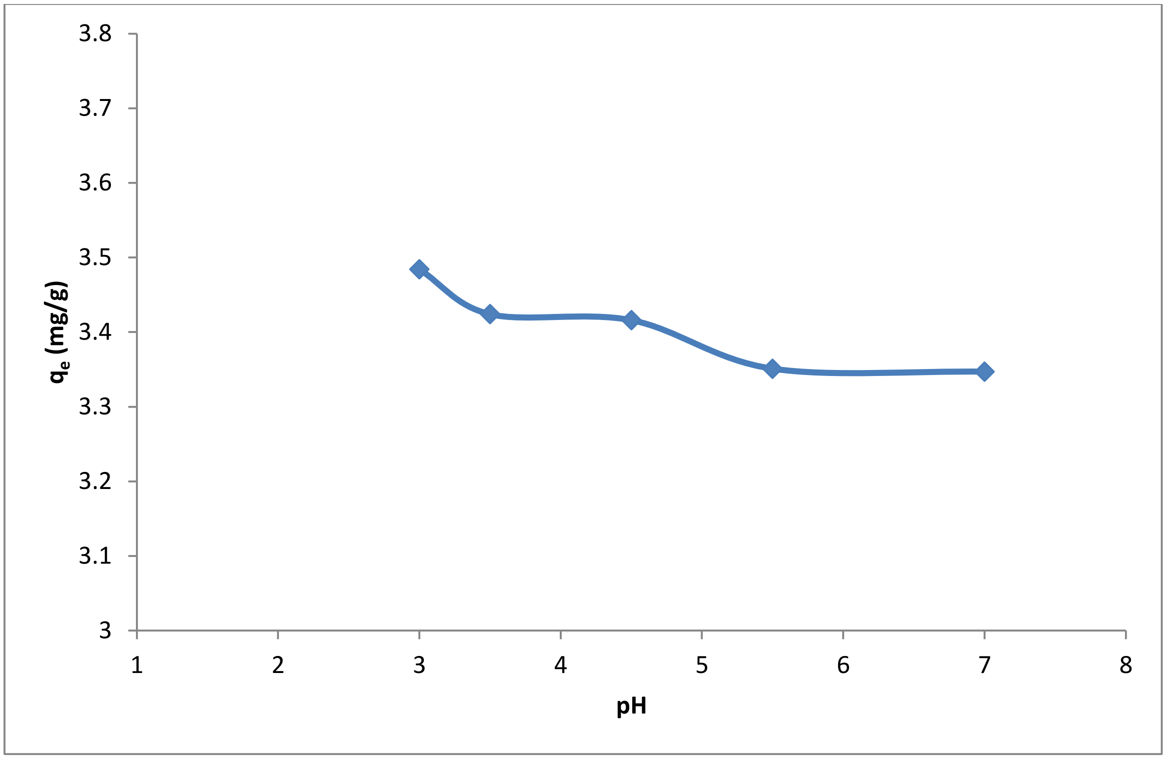


Fig. 12. plot of q_e vs pH

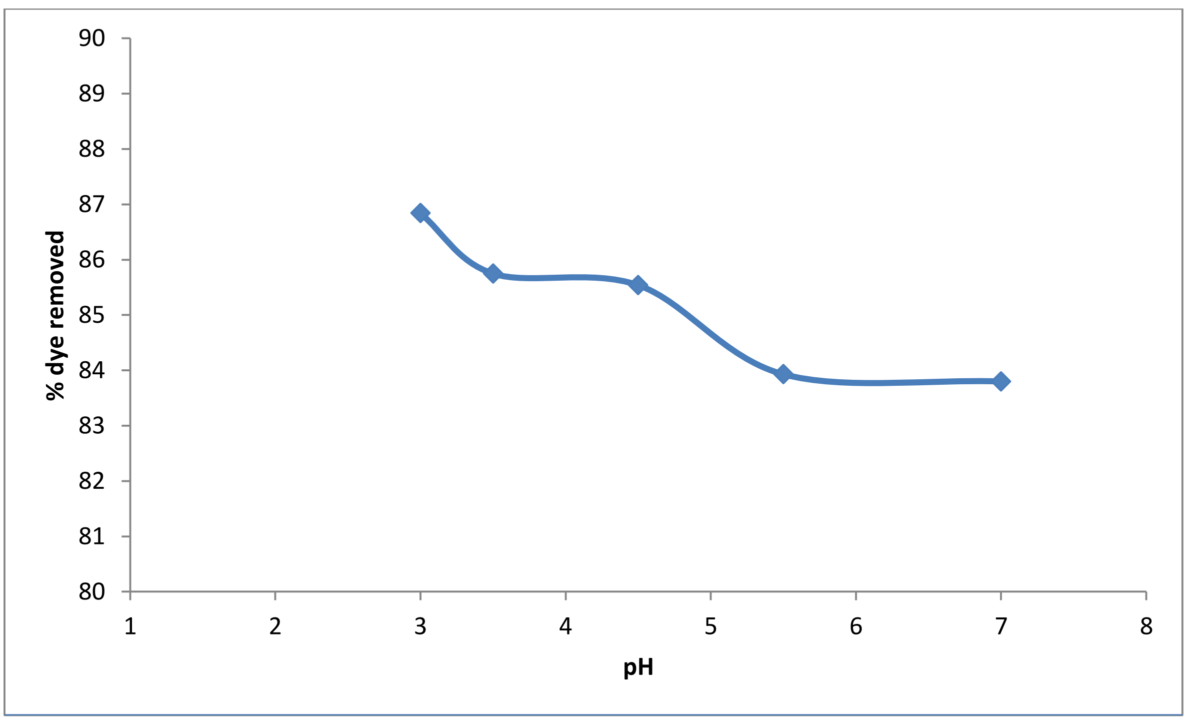


Fig 13. plot of % removal of dye vs pH

It was found that with decrease in pH the value of percentage of dye removed increased.

4.7 Wood dust modified with inorganic acids:

Pine wood was now treated with inorganic acids like HCl and H_2SO_4 in similar way as with Acetic acid. Natural Pine wood dust was mixed with 1M solution of inorganic acids in the ratio 1:10 (w/v). Slurry was stirred continuously for 30 minutes and then dried. Then the adsorption experiments were performed as done earlier.

Sample	Equilibrium concentration Ce (mg/l)	% of removal of dye
Natural Wood dust	20.074	74.86
Acetic acid modified wood dust	12.934	84.02
HCl modified wood dust	18.574	76.74
H_2SO_4 modified wood dust	17961	77.50

Table 7. Wood dust modified with different acids.

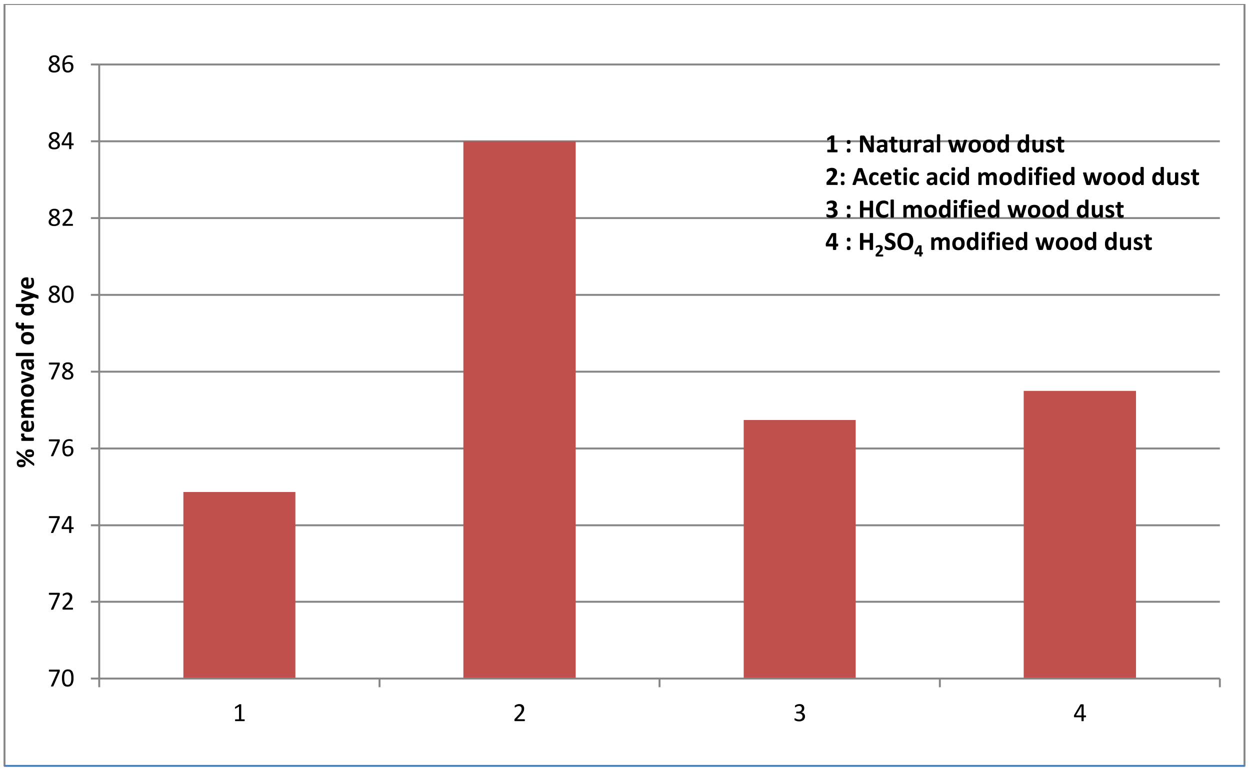


Fig 14. % removal of dye vs modified wood dust with different acids

It was observed that the use of inorganic acids enhanced the adsorption efficiency of Pine wood dust but the effect was not as great as with Acetic acid.

4.8 Effect of temperature:

Effect of temperature on adsorption efficiency of Acetic acid modified wood dust was studied.

Temperature (^oC)	C_e (mg/l)	% removal of dye
25	12.934	84.02
35	11.424	85.69
45	10.562	86.71

Table 8. Effect of temperature

It showed that with increase in temperature the adsorption capacity of the modified wood dust increased slightly. Hence it was clear that this adsorption process is endothermic in nature and adsorption of MB on Acetic acid modified wood dust was favorable at higher temperature.

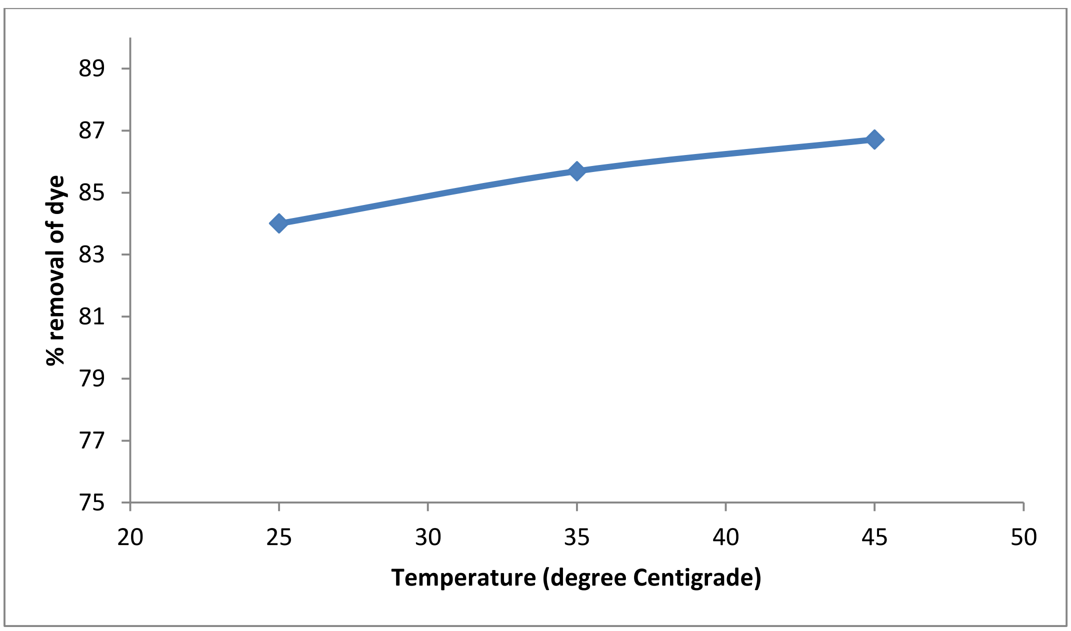


Fig 15. plot of %removal of dye vs temperature

Chapter 5

Conclusion

This study shows that Pine Wood dust is a very efficient adsorbent for Methylene Blue dye removal from its aqueous solution.

- Results showed that the adsorption efficiency of Pine Wood increased considerably when modified with Acetic acid.
- Adsorption efficiency of wood dust rose from 75% to 84% approximately with its modification with acetic acid.
- Results also showed that addition of electrolytes decreased the adsorption efficiency of Pine Wood dust.
- The adsorption process is endothermic in nature and is favorable at higher temperature. Adsorption efficiency of the Acetic acid modified wood dust increased with decrease in the pH of the solution.
- From isotherms it is clear that rate of adsorption of dye also increased with the modification of Pine Wood dust.

Thus, modified Pine wood dust with acetic acid can serve as an excellent combination for carrying out of Methylene Blue dye from Industries, thus reducing the effluent discharge problems from dye using Industries.

References:

Robinson T., McMullan G., Marchant R., Nigam P.;"Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. BioResource technology 77 (2001) 247 – 255.

Oladoja N A., Aboluwoye C O., Oladimeji Y B.; "Kinetics and Isotherm studies of Methylene Blue Adsorption onto Ground Palm Kernel Coat". Turkish J. Eng. Env. Sci. 32 (2008) 303 – 312.

Iqbal M J., Ashiq M N.; "Adsorption of dyes from aqueous solution on activated charcoal". Journal of Hazardous Materials B139 (2007) 57 – 66.

Fil B A., Ozmetin C., Korkmaz M.; "Cationic Dye (Methylene Blue) Removal from Aqueous solution by Montmorillonite". Bull. Korean Chem. Soc. 33 (2012) 3184 – 3190.

Auta M., Hameed B H.; "Acid modified local clay beads as effective low – cost adsorbent for dynamic adsorption of Methylene Blue". Journal of Industrial and Engineering Chemistry; DOI 10.1016j.jiec 2012 12.012 (2013)

Kansal S K., Singh M., Sud D.; "studies on photodegradation of two commercial dyes in aqueous phase using different photocatalyst". Journal of Hazardous Material 141 (2007) 581 – 590.

Guibal E., Roussy J.; "Coagulation and flocculation of dye – containing solutions using a biopolymer (Chitosan)". Reactive and Functional Polymers 67 (2007) 33 – 42.

Garg V K., Amita M., Kumar R., Gupta R.; "Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a timber industry waste". Dyes and Pigments 63 (2004) 243 – 250.

Conley R F., Lloyd M K.; "Adsorption studies on kaolinite –II Adsorption of Amines". Clays and Clay Minerals 19 (1971) 273 – 282.